



Contents lists available at ScienceDirect

Bioresource Technology

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Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 °C



Yongwoon Lee^a, Jinje Park^a, Changkook Ryu^{a,*}, Ki Seop Gang^{a,b}, Won Yang^b, Young-Kwon Park^c, Jinho Jung^d, Seunghun Hyun^d

^a School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, South Korea

^b Energy Systems R&D Group, Korea Institute of Industrial Technology, Cheonan 330-825, South Korea

^c School of Environmental Engineering, University of Seoul, Seoul 130-743, South Korea

^d Division of Environmental Science and Ecological Engineering, Korea University, Seoul 136-713, South Korea

HIGHLIGHTS

- Biochar yield of agricultural residues was dependant on the ash and lignin contents.
- Development of internal pores and surface area was different between biomass types.
- Biochar from wood and bagasse developed pores of various sizes and large surface area.
- The biochar became alkaline (pH 9.3–10.5), except for PKS biochar having a pH of 6.9.
- Dominant inorganic elements in biochar widely varied between biomass types.

ARTICLE INFO

Article history:

Available online 2 September 2013

Keywords:

Agricultural residues
Biomass
Biochar
Forestry residues
Slow pyrolysis

ABSTRACT

Application of biochar from biomass pyrolysis to soil is gaining greater interest; this can ameliorate the soil quality, reduce fertilizer consumption, and sequester carbon. This study compares the characteristics of biochar produced by slow pyrolysis at 500 °C for agricultural residues: sugarcane bagasse, cocopeat, paddy straw, palm kernel shell (PKS) and umbrella tree. In the biochar yield, the influence of the inert and lignin contents was significant. The wood stem, bagasse and paddy straw had biochar yields of 24–28 wt.% from the organic fraction while cocopeat had 46 wt.%. The carbon content of biochar ranged from 84 wt.% to 89 wt.%, which corresponded to 43–63% of carbon in the biomass. The biochar from wood stem and bagasse had well-developed pores of various sizes with large surface areas. Although the surface area was significant, PKS biochar had dense matrix with few large pores. The elemental composition and pH of biochars were also compared.

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1. Introduction

As the product of photosynthesis from carbon dioxide and water, biomass is the only renewable resource available for both energy and chemical feedstock production. Among different utilization methods of biomass, this study focuses on biochar, which is the solid product of pyrolysis. At moderately high temperature in an inert atmosphere, pyrolysis thermally decomposes the carbohydrate structure of biomass into carbonaceous solid residue (biochar), and condensable and non-condensable vapors of various molecular weight compounds. Biochar is a value-added product, which can be used for many purposes. It is highly carbonaceous and hence contains a high energy content, comparable to high rank

coals. In addition, the heterogeneous reaction of solid carbon with oxygen is slower than homogeneous oxidation, which is relatively safe and easy to control. For this reason, the primary use has been as fuel (charcoal) for heat production for cooking and heating. Biochar also has a large microscopic surface area due to the micropores developed during pyrolysis, and can be used for the filtration and adsorption of pollutants. Such feature of biochar can be further enhanced by physical or chemical activation, of which the final product is referred to as activated carbon.

Recently, the application of biochar to soil is drawing greater attention for sustainable soil quality improvement and carbon sequestration (Lehmann et al., 2006; Woolf et al., 2010; Sohi, 2012). In the soil, biochar increases the capacity of the soil holding water and nutrients, reducing the need for fertilizers. Many small and field tests reported increases in the plant growth and crop productivity after mixing biochar with the soil (Jeffery et al., 2011). Biochar also reduces the emission of other greenhouse gases from

* Corresponding author. Tel.: +82 31 299 4841; fax: +82 31 290 5889.

E-mail address: cryu@me.skku.ac.kr (C. Ryu).

the soil, such as N_2O and CH_4 (Van Zeeuwen et al., 2009). More importantly, biochar can directly store the carbon for a sufficiently long time due to its strong resistance to biological decomposition (Preston and Schmidt, 2006; Liang et al., 2008). This has been proved by research on the dark Amazonian soil called *terra preta* (Glaser et al., 2001; Lehmann et al., 2003). Since the carbon originates from atmospheric CO_2 , the application of biochar to soil can contribute to the mitigation of climate change (Lehmann et al., 2006). This can achieve a maximum of 12% reduction in current anthropogenic CO_2 emission without endangering food security, habitat or soil conservation (Woelf et al., 2010). In general, biochar needs to have high adsorption and cation exchange capacities, and a small amount of mobile compounds such as tar (Glaser et al., 2002; Liang et al., 2008). However, the effects of biochar and the requirements on its properties for soil amendment have not fully been established (Manyà, 2012). This is because they are influenced by numerous parameters including raw biomass types, pyrolysis conditions, soil properties, and complex mechanisms involved for plant growth.

Although raw biomass consists of carbohydrates produced from photosynthesis, detailed structures and compounds widely vary, depending on the type of plants and the sections in a plant. The process conditions of pyrolysis also significantly influence the properties of biochar (Antal and Grønli, 2003). The process parameters include the temperature, heating rate, pressure, purge gas and particle size. In general, higher temperature, large heating rate, lower pressure or smaller particle sizes promote the decomposition of biomass polymers, and increase the release of pyrolytic vapors from the solid. Therefore, these conditions influence the yield, carbon content, surface area, pore volumes and other properties of biochar. Pyrolysis conditions can also be adjusted to maximize the release of condensable vapors to produce bio-oil, which is referred to as fast pyrolysis (Mohan et al., 2006). In order to achieve a heating rate of about $100\text{ }^\circ\text{C/s}$ or higher, fast pyrolysis is typically performed in a fluidized bed for large heat transfer coefficient, and requires a size reduction of feedstock to about 1 mm for immediate intra-particle heating. In fast pyrolysis, biochar is sometimes used as the source for the heat required to maintain a reactor temperature of about $500\text{ }^\circ\text{C}$. Compared to fast pyrolysis, slow pyrolysis is ideal for biochar production, since it increases the yield of biochar. It can be performed at various scales by a simple heating process without specific requirements for particle size reduction.

This study investigates the properties of biochar by slow pyrolysis for five forestry and agricultural residues from Indonesia: sugarcane bagasse, cocopeat, paddy straw, palm kernel shell (PKS), and umbrella tree. A representative reaction temperature of $500\text{ }^\circ\text{C}$ was selected for pyrolysis in this study, which is high enough to complete the thermal decomposition of the two main constituents (cellulose and hemicellulose) of land biomass. Detailed properties of biochar from the samples were compared for the mass yield, elemental composition, surface area, morphology, pH and ash content. Based on the results, the utilization of the biomass residues for biochar production was discussed.

2. Methods

2.1. Biomass samples

The properties of biochar were studied for six biomass residues delivered from Indonesia after air-drying. Bagasse is the fibrous residue of sugarcane stalks, after crushing for sugar production. Cocopeat is the powdered by-product of coconut production from coconut husks. Its particle size is less than 1 mm. Paddy straw (*Oryza sativa*) is the residue of the plant species commonly referred to as long-grained rice. Palm kernel shell (PKS) is the hard shell

residue left after the nut has been crushed for palm oil extraction. Its particle size is typically about 1–2 cm. The raw PKS sample contained pebbles of similar sizes, which were segregated before analytical and pyrolysis tests. The wood stem and bark used in this study are the residues of the sawmill processing of Umbrella tree (*Maesopsis eminii*) for the production of timber. The two parts of the tree were manually separated for individual characterization and pyrolysis experiments due to the differences in the chemical composition and pyrolysis characteristics.

2.2. Slow pyrolysis tests

Fig. 1 shows a schematic diagram of the bench-scale fixed bed reactor used for slow pyrolysis. The reactor was made of stainless steel with a diameter of 10 cm and a height of 30 cm, and placed inside an electrically-heated furnace. In each test, 100–400 g of sample was heated from room temperature to $500\text{ }^\circ\text{C}$ at approximately $10\text{ }^\circ\text{C/min}$, and maintained for at least 1 h to allow sufficient time for complete pyrolysis. Note that a pyrolysis temperature of $500\text{ }^\circ\text{C}$ was selected as an indicative temperature for comparison of biochar properties. Pyrolysis at lower temperatures would yield a larger amount of biochar. However, the key properties of biochar, such as pore structures and surface area, sufficiently develop at around $500\text{ }^\circ\text{C}$ (Lee et al., 2013) by the complete thermal decomposition of cellulose and hemicellulose. In the application to soil by pot trials (Rajkovich et al., 2012), the growth of corns was the highest for biochar produced at a temperature of $500\text{ }^\circ\text{C}$ although the effects of feedstock types were much larger.

The pyrolysis vapor purged by nitrogen (1.5 l/min) passes through a series of condensers for collection of condensable products (bio-oil including water). The composition of the non-condensable gas species was measured using a gas analyzer, and periodically sampled for a gas chromatograph. A detailed description of the process and analytical methods has been presented elsewhere (Lee et al., 2013).

2.3. Analysis of biomass and biochar

The proximate analysis of raw biomass and biochar was based on the ASTM standards (moisture content: ASTM E871-82, ash: ASTM D1102-84, volatile matter: ASTM E872-82 and fixed carbon is calculated by difference). The ultimate analysis for C, H, and N contents was carried out using an elemental analyzer (CE Instruments, EA 1108), and the O content was calculated by difference.

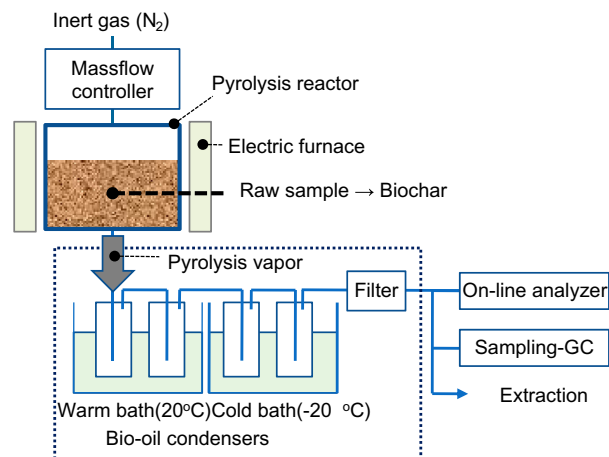


Fig. 1. Schematic of the slow pyrolysis reactor.

Table 1

Characterization of air-dried biomass samples.

Biomass		Bagasse	Cocopeat	Paddy straw	PKS	Wood stem	Wood bark
Proximate analysis (wt.%)	Moisture	13.2	21.0	7.3	11.9	8.8	10
	VM ^a	71.0	49.1	56.4	66.8	80.1	68.9
	FC ^{b,c}	13.7	25.3	15.4	17.9	10.7	16.2
	Ash	2.1	4.6	20.9	3.4	0.4	4.9
	VM/FC	5.14	1.93	3.66	3.73	7.46	4.25
Ultimate analysis (wt.% daf)	C	51.71	61.57	48.75	55.82	50.52	53.42
	H	5.32	4.37	5.98	5.62	5.81	6.12
	O ^c	42.64	33.04	43.28	37.73	43.44	39.06
	N	0.33	1.02	1.99	0.84	0.23	1.40
HHV (MJ/kg)		17.02	16.54	13.45	15.89	16.46	15.40

^a VM: volatile matter.^b FC: fixed carbon.^c By difference.

For the detailed investigation of the weight loss characteristics during pyrolysis, thermogravimetric analysis (TGA) was carried out for the raw biomass samples. For about 10 mg of fine powders, a TGA analyzer (Shinco, TGA N-1000) was used to measure the sample weight while being heated at a rate of 20 °C/min from a room temperature to 800 °C, under a nitrogen flow rate of 30 ml/min. The recorded weight loss history was normalized for the initial weight, and its rate was calculated.

For the pH measurement, biochar to deionized water ratios from 1:5 to 1:20 (wt.:wt.) are used in literature (Singh et al., 2010; Yuan et al., 2011; Wu et al., 2012). In this study, 1:10 wt.:wt. ratio was used to form homogeneous suspension, and the pH was determined after 1 h of equilibration using an Orion PH meter (Thermo Scientific).

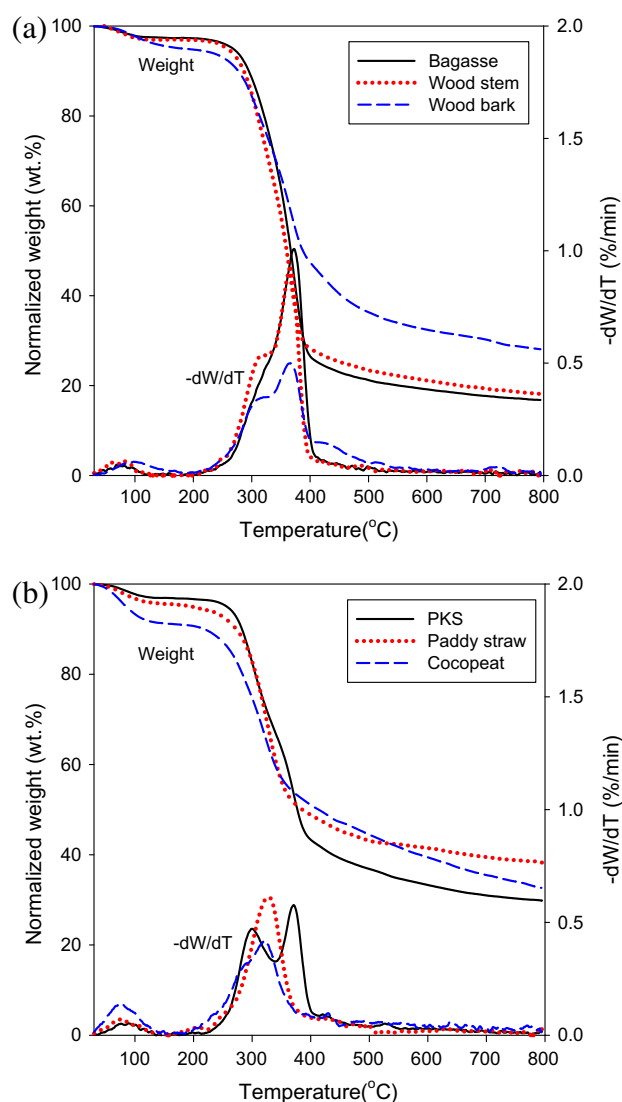
The microscopic surface area of biochar was measured by using the N₂-BET method (Micrometrics, Tristar 3020). The surface morphology of biochar was investigated using scanning electron microscopy (SEM, JEOL JSM-7600F). The distribution of pore volumes in biochar was measured using a porosimeter (Micromeritics, AutoPore 4 9250) for the pores in the range of 10 nm–100 μm.

3. Results and discussion

3.1. Biomass characterization

Table 1 compares the characteristics of air-dried biomass samples. The biomass samples exhibited large variations in the proximate analysis, especially in the ash content. Paddy straw contained the highest ash content (20.9%), most of which was found to be SiO₂ (Si 78,640 ppm, followed by K 11,650 ppm and Ca 3229 ppm). The rest of the samples had an ash content below 5%. The stem part of the umbrella tree had the lowest (0.4%) while its bark had a relatively high ash content (4.9%). For the moisture content, cocopeat had the highest moisture content. It also had the lowest VM content (VM/FC ratio: 1.93) and the highest carbon content (61.57%), which implies that the biochar yield would be the largest among the samples.

Fig. 2 shows the TGA curves of the samples. The thermal decomposition actively took place below 500 °C, having one or two distinct peaks between 290 °C and 370 °C. For the two distinct peaks, the first peak corresponded to the decomposition of hemicellulose and the second to cellulose (Yang et al., 2007; Cagnon et al., 2009). Hemicellulose, cellulose and lignin are the three main polymer constituents of land biomass, but their chemical structures and corresponding thermal stability differ. Also, their proportions vary widely between biomass types and parts. Cellulose and hemicellulose consisting of simple sugar monomers decompose at temperatures lower than 450 °C, mostly into light molecular

**Fig. 2.** TGA results of biomass samples.

weight compounds to be released as pyrolytic vapors. In contrast, lignin is an amorphous and hydrophobic polymer with a huge molecular weight in excess of 10,000 g/mol, consisting of numerous functional groups containing aromatic sub-structures of carbon. During pyrolysis, lignin slowly decomposes over a wide

Table 2

Product yields of pyrolysis at 500 °C.

Biomass		Bagasse	Cocopeat	Paddy straw	PKS	Wood stem	Wood bark
Air-dried basis (wt.%)	Biochar	24.5	38.7	41.0	32.2	22.3	31.9
	Bio-oil	55.1	39.1	37.2	51.4	59.5	50.5
	Gas ^a	20.4	22.2	21.8	16.4	18.2	17.6
Dry ash-free basis (wt.%)	Biochar	26.4	45.9	28.0	34.0	24.1	31.7
	Bio-oil	49.5	24.3	41.6	46.6	55.9	47.6
	Gas	24.1	29.8	30.4	19.4	20.0	20.7

^a By difference.**Table 3**

Summary of biochar properties produced at 500 °C.

Biomass		Bagasse	Cocopeat	Paddy straw	PKS	Wood stem	Wood bark
Proximate analysis (wt.%)	Moisture	1.3	2.55	2.07	0	1.46	0.36
	VM	9.17	14.30	6.46	12.29	12.79	18.14
	FC ^a	80.97	67.25	39.10	80.85	83.47	68.66
	Ash	8.57	15.90	52.37	6.86	2.28	12.84
	VM/FC	0.11	0.21	0.17	0.15	0.15	0.26
Ultimate analysis (wt.% daf)	C	85.59	84.44	86.28	87.85	89.31	84.84
	H	2.82	2.88	3.12	2.91	2.57	3.13
	O ^a	10.48	11.67	7.35	8.14	7.34	10.20
	N	1.11	1.02	3.25	1.11	0.78	1.83
Carbon yield (wt.%)		43.7	62.9	49.6	53.5	42.6	50.3
Inorganic elements ^b (ppmw)	Al	1627	3436	2653	4275	328	6588
	Ca	1798	2667	6018	392	1674	19,730
	Fe	1276	2088	1956	21,380	241	4736
	K	2643	22,960	21,340	1219	2018	6470
	Mg	390	554	2976	131	190	1111
	Mn	104	33	1560	35	40	221
	Na	336	13,710	753	534	114	30
	P	504	302	3367	274	134	485
	Si	19,460	11,590	176,020	10,310	1052	7604
	Ti	460	507	339	230	171	615
N ₂ -BET area (m ² /g)		202	13.7	45.8	191	316	13.6
pH		9.3	10.3	10.5	6.9	9.5	9.6

^a By difference.^b Listed for elements above 200 ppmw.

range of temperature and contributes more to the formation of biochar, leaving condensed aromatic carbons with reduced functional groups. Cagnon et al. (2009) reported that the char yield is 23.5% for hemicellulose, 19% for cellulose and 45% for lignin. The TGA results in Fig. 2 clearly showed that the pyrolysis temperature of 500 °C chosen in this study for biochar production was sufficiently high enough for comparison of the representative properties between biochar samples. The results also implied that the biochar yields from slow pyrolysis tests would vary significantly between samples.

3.2. Product yields of pyrolysis

Table 2 lists the mass yield of pyrolysis products produced at 500 °C using the bench-scale reactor. The biochar yields for wood stem and bagasse were about 22–25%, but those of paddy straw and cocopeat were significantly higher (~40%). The biochar yields were in reasonable agreement with the relative weight at 500 °C in the TGA curves (Fig. 2). The bio-oil yields (including the water condensed) were over 50% except for cocopeat and paddy straw. One reason for the large differences in the product yields was the inorganic and water in the raw samples, which were added to the biochar and bio-oil, respectively. Note that, in Table 1, the ash content of paddy straw was as high as 20.9% and the moisture content of cocopeat was 21.0%.

In order to remove the effect of moisture and ash, the bio-oil and biochar yields were expressed into a dry ash free (daf) basis, as follows:

$$Y_{\text{biochar,daf}} (\text{wt.\% daf}) = 100 \times (Y_{\text{biochar,ad}} - A) / (100 - M - A)$$

$$Y_{\text{bio-oil,daf}} (\text{wt.\% daf}) = 100 \times (Y_{\text{bio-oil,ad}} - M) / (100 - M - A)$$

where $Y_{\text{biochar,ad}}$ and $Y_{\text{bio-oil,ad}}$ (wt.%) represent the air-dried basis yields of biochar and bio-oil, respectively. M and A (wt.%) are the moisture and ash contents of biomass, respectively. For example, the biochar yield of paddy straw on a daf basis is $100 \times (41.0 - 20.9) / (100 - 7.3 - 20.9) = 28.0 \text{ wt.\% daf}$. The results are also listed in Table 2. The biochar yield from the organic portion of paddy straw was in fact similar to those of wood stem and bagasse. Such biochar yield is typical for lignocellulosic biomass. In contrast, the biochar yields of cocopeat and PKS were considerably higher. These two samples are from the storage tissue of biomass that contains a larger proportion of lignin. Coconut shell has been reported to have a lignin content as high as 46 wt.% (Cagnon et al., 2009) and PKS 46–51% (Kim et al., 2010; Sabil et al., 2013). The wood bark had about 8% higher biochar yield than the stem part due to the increase of lignin and other polymers. In Jin et al.'s study (2013), barks of two hard woods (oak and poplar) had cellulose and hemicellulose contents of approximately 30% and 20%, respectively, which were considerably lower than those of sapwood parts.

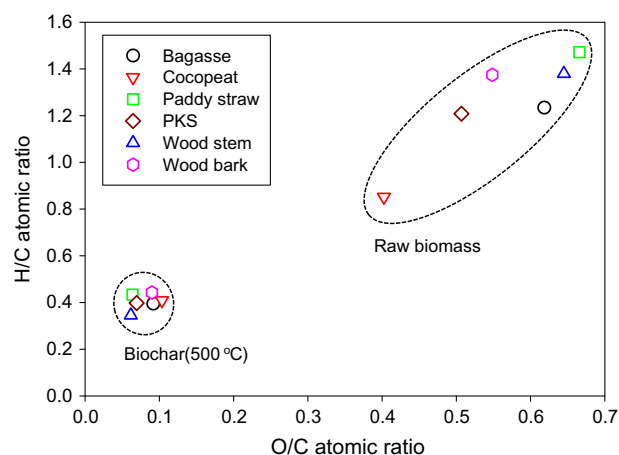


Fig. 3. Van Krevelen diagram of biomass and biochar.

Instead, lignin and other extractives increased by about 6–8% and 18–24%, respectively.

3.3. Characteristics of biochar

Table 3 summarizes the properties of biochar produced at 500 °C. The VM/FC ratio decreased to less than 0.26 as the result of pyrolysis. Therefore, the biochar products became highly resistant to further decomposition, biological as well as thermal. Among the samples, cocopeat and wood bark had a relatively high VM/FC ratio (0.21 and 0.26, respectively). Therefore, the mass yield of biochar above the pyrolysis temperature of 500 °C would be larger for the two samples. This agreed with the trends in the TGA curves shown in Fig. 2. The ash content of biochar was very high for paddy straw (52.37%), which was inherited from the raw samples.

Table 3 also lists the results of ultimate analysis. The solid residue became highly carbonaceous, with a carbon content ranging from 84% to 89%. The C, H and O composition of the raw biomass and biochar were compared on a van Krevelen diagram shown in Fig. 3. In contrast to the large variation between the raw biomass samples, the biochars became similar in terms of the elemental composition.

From the carbon content and mass yield, the carbon yield representing the amount of carbon remaining in the biochar was calculated. Bagasse and wood stem had carbon yields of about 43% while the rest had values in the range of 50–63%.

Table 3 also lists the concentrations of inorganic elements in the biochars. Ca, Si, Al and K were common elements in biochar, but their concentrations had large differences between samples. Si was dominant in the biochar of paddy straw (176,020 ppm) and bagasse (19,460 ppm) followed by K (21,340 and 2640 ppm, respectively). Note that the straw biochar had an ash content of over 50%. Cocopeat biochar was rich in K and Na. PKS biochar had the largest concentration of Fe among the samples. Wood stem contained K, Ca and Si in similar concentrations (1000–2000 ppm), of which the values were lower than for the other samples due to the low ash content. In contrast, Ca was dominant in the bark, which has also been reported for the barks of other trees (Jin et al., 2013).

The pH is an important property of the soil, which influences the types of plants and microbes to thrive, and the availability of nutrients to be absorbed. Soil acidification is the result of nitric acid and sulfuric acid from fossil-fuel combustion (Reuss and Johnson, 1985) and the long-term application of nitrogen compounds fertilizers (Malhi et al., 1998). Neutralizing acid soils by applying biochar can improve the soil quality, and increase the productivity of crops. As also listed in Table 3, the biochar tended to be highly

alkaline (pH 9.3–10.5), except for PKS (pH 6.9). The alkalinity of biochar is influenced by three factors: (i) organic functional groups, (ii) carbonates, and (iii) inorganic alkalis (Yuan et al., 2011; Fidel et al., 2012). The contribution of organic functional groups such as –COOH and –OH is known to decrease with increasing pyrolysis temperature by progress of thermal decomposition. In contrast, the contribution of carbonates formation (such as CaCO₃ and MgCO₃) and inorganic alkalis (such as Na and K) becomes important above 500 °C (Yuan et al., 2011). As a result, higher pyrolysis temperatures significantly increased the pH of biochar (Spokas et al., 2012; Wu et al., 2012; Kim et al., 2013). The organic functional groups in the biochar samples were not analyzed in this study. However, it can be easily identified in Table 3 that the PKS biochar had the lowest concentrations of alkali and alkali-earth elements such as Na, K, Ca, and Mg. This could be the main reason for the lowest pH of the PKS biochar.

One of the main roles of biochar in the soil is to provide the increased retention of nutrients in addition to the direct supply of nutrients. Therefore, the microscopic surface area is one of the crucial properties for biochar, which determines the capability of nutrients and water adsorption. The N₂-BET surface area of biochar by small pores of 2–50 nm is listed in Table 3. It had a wide variation between biochar samples. The biochar from wood stem, sugarcane bagasse and PKS developed large microscopic surface area over 190 m²/g. In contrast, the surface area of cocopeat and wood bark was less than 15 m²/g. The value for paddy straw was also insignificant.

The formation of pores in the biochar can also be investigated by SEM and pore volume distribution. The SEM images of biochar are presented in Fig. S1 of the Supporting Info. The biochar from bagasse (Supplementary Fig. S1a) and the inner stem of umbrella tree residue (Fig. S1e) had longitudinal pores in sizes ranging from about 10–50 μm. These large pores originated from the vascular structure of the raw biomass. The thermal decomposition of cellulose and hemicellulose has left the cell walls which typically contain a larger proportion of lignin. The large pores identifiable in the SEM images play an important role, when applied to the soil. They can provide habitats for symbiotic microorganisms such as bacteria (0.3–3 μm), fungi (2–80 μm) and protozoa (7–30 μm) (Thies and Rillig, 2009). Such large pores are not directly related to the microscopic surface area in Table 3, since the surface area is determined by meso- and micropores. However, the large pores can act as routes of pyrolytic vapors to be easily released from inner parts, and provide a matrix on which smaller pores develop. Although not seen in the figure, the cross-sectional surfaces of bagasse biochar contained numerous holes of less than 1 μm spread all over the surfaces. The biochar of the wood bark (Fig. S1f) consisted of irregular surfaces without the vascular structures. In contrast, cocopeat biochar (Fig. S1b) had fractured pieces as a result of coconut processing, and each piece had smooth surfaces that were unlikely to develop small pores on them. The biochar of paddy straw (Fig. S1c) consisted of thin-walled plates exhibiting marks of vascular structures. However, it did not have large cylindrical pores inside, unlike the biochar of bagasse and the wood stem. PKS biochar (Fig. S1d) had the most dense and compact structure with a few small pores of about 1 μm.

Fig. 4 plots the pore volume distribution measured for pores ranging from 10 nm to 100 μm. Bagasse had many pores in various sizes. Cocopeat biochar had pores only of >1 μm with over 3.0 mL/g (outside the y-axis range), which should be the voids between the powdered particles rather than pores inside particles. In the biochar of paddy straw, no small pores were developed while the volume of large pores over 0.1 μm was significant. Due to the dense matrix observed in the SEM image, PKS biochar only had some meso-pores formed around 10 nm or smaller. This explains the large surface area of the biochar.

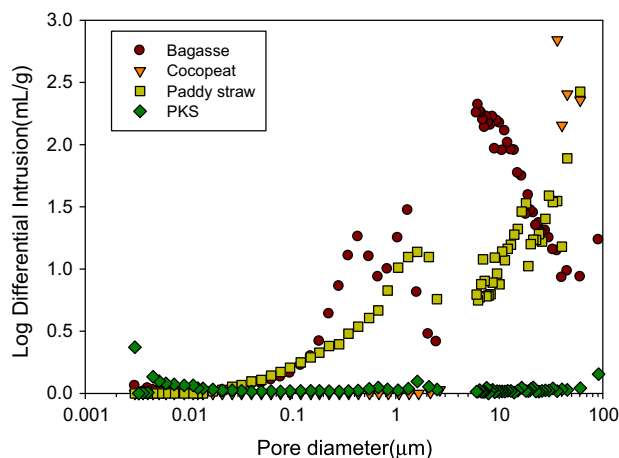


Fig. 4. Distribution of pore volume in biochar.

Considering the specific surface area and pore development, raw biomass materials having vascular structures such as bagasse and wood were favorable for the quality of biochar. Although the biochar yield was lower than for the other samples, bagasse and wood stem developed pores of various sizes including micropores leading to a larger surface area. Despite the largest mass yield, cocopeat biochar had low specific surface area. In contrast, PKS biochar had a large surface area but did not develop large pores. The surface area and pore volumes can be enhanced physically (endothermic gasification using steam or CO₂ at temperatures typically above 800 °C) or chemically. For example, the PKS biochar activated at 900 °C using steam has a surface area of over 1000 m²/g (Lua and Jia, 2009). Such processes are intended for the production of activated carbon as an adsorbent of pollutants. However, the activation of char requires much greater energy and cost input compared to the slow pyrolysis process, which would significantly increase the cost of biochar products.

4. Conclusions

Biochar produced from the pyrolysis of five biomass samples at 500 °C had different physical and chemical properties. Biochar yield was significantly influenced by the ash and lignin contents of biomass. Biochar from wood stem and bagasse developed pores of various sizes that were favorable for soil application. Other biochar samples had low surface areas or poor development of large pores. While biochars became highly carbonaceous, dominant inorganic elements widely varied between samples. The pH of biochar was 9.3–10.5, except for PKS. These results can be used to establish ideal utilization routes of biomass for energy and/or biochar production.

Acknowledgements

This work was performed with the financial support of the Cooperative Research Program for Agriculture Science & Technology Development (Project No. PJ0079662011), Rural Development Administration (RDA), Republic of Korea. The biomass samples were provided by the R&D program of the Korea Institute of Industrial Technology (Grant No. EO-13-0010).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2013.08.135>.

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